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# FINAL REPORT

on

A Facility for the Attribute-Based Vapor Phase Processing  
of Multilayers and Coatings

Department of the Navy

N00014-95-1-1098

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June 26, 1997

## SUMMARY

An electron beam deposition system suitable for the intelligent processing of oxide films and coatings has been designed and constructed. The three major features include (i) a heated substrate with a rotating stage (ii) magnetically rastered e-beam dual sources, (iii) four sub-systems for measuring film properties either in situ or post situ. The latter include: (a) an infrared imaging system, (b) a beam curvature apparatus for stress measurement, (c) an atomic force microscope to quantify topography.

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## I. VAPOR-DEPOSITED FILMS AND COATINGS

### I.1 Process Description and Performance Goals

Physical Vapor Deposition (PVD) is the generic term used for processes wherein a solid film is grown by condensation of a vapor produced by thermal *evaporation* or *sputtering*. There are numerous variants of PVD processes but each can be viewed as consisting of three basic steps.

- *Vapor Generation*, wherein atoms or molecules from a solid source are energized into vapor by momentum transfer of high energy ions, or by thermal activation.
- *Vapor Transport*, which involves primarily the expansion of the vapor cloud away from the source, but often includes physical or chemical interactions with injected gases (or contaminants).
- *Vapor Deposition* on a Substrate to produce a film with the desired macro- and micro-structural features and residual stress levels.

It is convenient for sensing and control purposes to visualize a PVD system as a set of three *interconnected* subsystems corresponding to the above steps, each with specific functions, performance metrics, modeling and sensing requirements, and control parameters which may be varied, independently or in combination, to achieve the desired performance goals of the process.

The quality descriptors are either *physical* (thickness, conformality, residual stress, surface quality), *chemical* (bulk and interfacial ) or *microstructural* (grain structure/size/aspect ratio, texture, porosity, second phases). The goal of the system is to develop the science base needed to implement a control strategy based on in situ monitoring of key product characteristics, especially those related to microstructure.

Economic considerations demand high productivity and an emphasis on sources capable of high vapor generation and deposition rates, especially for the thicker coatings and free standing foils of interest in structural applications. Electron beam evaporation is preferred. The higher rates add complexity to the task of balancing quality and yield as well as providing an ideal challenge for process control.

## **I.2 Processing Issues**

The deposition scenario involves arrival of the species to the growth front, adsorption, surface diffusion, attachment or desorption, and bulk diffusion. These phenomena are thermally activated, making homologous temperature ( $T/T_M$ ) the dominant parameter in controlling the evolving microstructure and the intrinsic residual strain. The thermal energy of the species is often insufficient to provide the desired level of surface mobility. Controlled active heating is preferred. Exogenous thermal loads also arise, associated with radiation and/or secondary electron bombardment from the sources. Temperature sensing and control are thus complex issues, requiring an understanding of the interplay between the various energy sources and sinks, as well as reliable models relating thermal history to microstructural evolution and residual strain.

The performance requirement of the vapor source is the attainment of the desired evaporation rate with a steady-state chemistry. The vapor energy, flow pattern and density distribution are prescribed by the source, but may be subsequently modified in the transport subsystem. In industrial practice, a high power electron-beam ( $>100kW$ ), is focused and rapidly scanned over the surface of a melt pool which is fed through the bottom by a solid ingot of the desired composition. Passage of the beam over a point on the surface leads to sharp transients in the local temperature and evaporation rate. The local burst of evaporation produces a recoil pressure which creates an inward bulge or "crater" on the molten surface, as well as a small plasma volume. Increasing the power density enhances the local thermal excursion and evaporation rate, as well as the ability of the beam to penetrate the vapor cloud without excessive energy losses. However,

higher power densities increase surface distortion, eventually leading to crater collapse and undesirable melt splashing, as well as cracking of the ingot. Thermal excursions must be tailored by suitable control of the beam power density and scanning rate to achieve an optimal combination of evaporation rate and energy efficiency, while avoiding splashing and cracking.

Steady-state operation requires that the vapor and feedstock chemistries, as well as the ingot feeding and evaporation rates, be identical. This poses challenges to the energy management of the source. For example, power density adjustments made to compensate for a perturbation in vapor chemistry or evaporation rate induce transients in the melt volume and, hence, its chemistry and that of the vapor. There is also an initial preconditioning transient that depends on the concentrations and partial pressures of the components.

A realistic description of the deposit subsystem is the ultimate goal. Transport modeling provides a quantitative description of the evolution of the temperature profiles in the substrate and on the deposit, as affected by (i) radiative heat transfer, (ii) conduction in the substrate and in the deposit, (iii) heat transfer due to condensation. Precise predictions of the deposit temperature play an important role. Also, information on the rate and spatial distribution of deposition upon the substrate are needed as input for microstructural modeling.

### **I.3 Microstructure and Residual Stress**

A microstructure-based control strategy requires not only an integrated understanding of the macro- and micromechanisms involved, but also quantitative relationships linking key microstructural features to process parameters. There is a wealth of literature on detailed micromodeling of thin film growth phenomena which has been invaluable in providing understanding and identifying relevant variables, but has had limited potential for prediction and control of microstructures. A more practical tool has been the concept of Zone Models (Fig.1) which are essentially processing maps relating deposit characteristics such as grain morphology and porosity, to homologous temperature and gas pressure. These models are experimentally-based but have a sound physical foundation, reflecting the competition between the relevant micromechanisms. They can be used to identify processing windows where the desired microstructures can be produced.

The goal is to build upon the Zone Model concept to develop processing maps which reflect those functional relationships deemed necessary for the control strategy. Emphasis is placed in the evolution of porosity, grain structure and residual stress. The variables affecting porosity are  $T/T_M$  (as it affects the diffusivities) and the deposition rate. The AFM has been acquired to experimentally characterize porous films in order to calibrate and validate the models. Grain sizes and orientations are controlled by three fundamental processes (i) crystal nucleation; (ii) crystal growth; and (iii) grain growth. The nucleation and growth stages involve formation of individual crystals which grow until they impinge and coalesce, leading to the formation of a continuous film and the generation of residual stress. Grain growth may then occur, driven by the reduction of the energies of the grain boundaries and film-substrate interface. Experimental calibration of nucleation densities and of the diffusivities is essential. These experiments are enabled by the new facility.

Grain boundaries are regions of low density compared to grain interiors. Grain growth therefore leads to a densification that can generate "intrinsic" residual tensile stresses. Other phenomena also result in "intrinsic" stress. A major effort in the new facility is aimed at understanding and controlling such stresses. For this purpose, the new unit is equipped with stress monitors.

Thermal residual stresses which occur when the temperature is changed superpose onto the intrinsic stresses. When the materials involved are elastic, these stresses are calculated in a straightforward manner, from the misfit stress. Yielding and creep change the residual stress. These behaviors are sensitive to the microstructure, particularly the grain size, and the layer thickness. The effects of film thickness on yield strength are not understood and will be studied using the new system.

## II. PVD SYSTEM DESCRIPTION

The electron beam deposition unit depicted in Fig. 2 has been constructed. It has several essential elements associated with source (Fig. 3) and the substrate (Fig. 4). It has ports that enable a range of sensors to be introduced. These sensors include: (1) an infrared camera to measure temperature distributions, (2) a laser interferometer to measure intrinsic residual strain by using a beam curvature method, (3) quartz oscillators to measure total fluxes, (4) standard pressure monitors and thermocouples.

The control of the deposition is achieved by an electron beam system with infrared heaters. The former creates vapor at the source in a well controlled manner. The latter is used for active heating of the film, as it deposits, in order to control the microstructure and the intrinsic residual strain. The source beam is equipped with programmable magnetic lenses that raster the beam of the source and change the focus. This feature enables adjustment of the power density as a primary means for controlling the evaporation rate and the temperature distribution. The substrate is equipped with a rotation stage having programmable rotation speed. This emulates commercial units used to coat parts having cylindrical geometry. The unit is equipped with dual sources and a shuttering system. An activated oxygen source is included for control of the oxygen partial pressure when oxides are being deposited.

A post situ capability for high spatial resolution surface characterization, by atomic force microscope (AFM) has also been acquired. The AFM enables topographic information to be obtained with unprecedented height resolution (in the nm range). This information is essential to the characterization of the nucleation stages of film formation. It also provides critical information about surface redistribution as deposition proceeds. The high resolution of the AFM is also essential to the characterization of the surfaces created when interfaces *decohere*. This knowledge is needed in the mechanisms identification phase of the modeling of the decohesion energy and in its consequent application in fail-safe design.

The new system is dedicated to process control-related research, including sensor assessment and analysis, identification experiments for control models, control-oriented model validation. It is being used for implementation of control strategies to produce films suitable for performance-related research. The design flexibility built into the new unit enables long lifetime (>10 years) by enabling new sensors and controllers to be added as they become available. The new facility is maintained by technician support provided by the Gordon McKay laboratory. The technician maintains the facility and trains users to ensure proper and efficient usage.

### **III. SUB-SYSTEM DESCRIPTIONS**

#### **III.1 Infrared Imaging**

A high resolution infrared imaging system has been integrated into the facility for in situ detection of surface micro-flaws ( $\sim 30\mu\text{m}$ ). The imaging system is composed of a snap shot Amber Galileo IR camera, an IR microscope objective with filter wheel and a synchronized control for digital image grabbing and processing. This system is tailored for imaging very low emissivity surfaces ( $<0.03$  or polished metals) through fast integration time ( $2\mu\text{s}/\text{frame}$ ). The special filter wheel permits an extended range of temperature measurements. The IR lens has a 100mm working distance to facilitate the imaging of extremely hot surfaces. The image processing tools allow synchronized image averaging to follow the induced heating pattern associated with a given loading history.

#### **III.2 Scanning Probe (Atomic Force) Microscopy**

A Digital Instruments Dimension 3000 Scanning Probe (Atomic Force) Microscope has been acquired. This instrument, in addition to generating topographic data with nanometer resolution, is configured with the following capabilities: (1) Tapping Mode imaging - a method of scanning the surface without dragging the probe across the surface. This is of critical importance for imaging cracks or features with sharp ledges without imaging distortions; (2) nanoindentation and hardness testing capabilities; (3) Force Modulation imaging - a capability for detecting phases of different elastic properties; (4) lateral and Chemical Force microscopy - a capability for measuring friction and adhesion properties; and (5) Scanning Thermal imaging - a capability for mapping thermal properties of surfaces at the nanoscale. This instrument provides necessary capabilities for determining the structure/processing/properties of films and coatings.

Acquisition of the microscope has involved working with Digital Instruments personnel to design a configuration modification to the microscope, necessary to accommodate a custom loading apparatus to be used in conjunction with the AFM/SPM. As originally planned, the modification consisted of installing a spacer to raise the SPM head, giving clearance for the loading stage to be placed under it. However, due to constraints on the design of a loading system (actuator size, specimen fixtures, etc.), and geometrical constraints on the existing scan head



clearance, the microscope modification involves two components: (1) raising the scan head through use of an appropriately sized spacer, and (2) creating clearance around the scan head by reconfiguring the head vertical motion system without disabling the integrated optics systems. Design of the loading apparatus and the microscope modification had to be approached in parallel. An illustration of the loading apparatus is included (Fig. 5). The modification design is complete, the microscope is currently being manufactured, and delivery and installation is expected prior to August 1, 1997.

### **III.3 Optical In Situ Curvature Measurement**

An optical curvature measurement system has been designed and constructed. The system is designed to measure, in situ, the change of radius of curvature of a bimaterial specimen as it is thermally cycled. The system is to be used in characterizing the thermal stresses in a thin-film/substrate system, such as thermal barrier coatings (TBCs) and diamond like coatings (DLCs). With the specially designed furnace, this system is able to measure growth stresses, etc.

To measure the curvature of the specimen, the system uses a scanning mirror to deflect a laser beam along the sample. The beam is deflected and strikes a position sensitive detector (PDS). The radius of curvature of the sample can be determined by the position of the incident beam on the PDS and the sample. The scanning mirror is controlled and the PSD is read by a program written with Labview. A schematic of the system is shown on figure 6. The system consists of the following:

(i) Vibration Isolation table: A vibration isolation table top includes a hole cut on one side to accommodate the furnace.

(ii) Laser Source: The light source is a Uniphase 110V, 5 mW (minimum output power), 632.8 nanometer (red wavelength) Helium-Neon laser. It has an outer diameter of 44.2 mm and a beam diameter of 0.81 mm. A beam shutter is used to control the emission of the laser beam.

(iii) Galvanometer Scanner is used to move the laser beam across the surface of the specimen. The scanner operates between  $\pm 5$  volts, with the capability of rotating  $\pm 20$  degrees. By supplying a voltage signal to the scanner, the scanning mirror can be rotated to the desired position at the desired velocity. A CX-660 Scanner Control Amplifier provides position control for the galvanometer.

(iv) Position Sensitive Detector (PSD): A Hamamatsu S1300 PSD with position signal amplifiers is used to detect the positions of the incident and reflected beams, from which the radius of curvature of the sample can be determined.

(v) LabVIEW: A program "*Radius Measurement*" has been written which operates and integrates the information.

(vi) Furnace: A top loading inert atmosphere furnace system (Model TC200, OxyGon Industries) has been specially designed and constructed to meet the most stringent specifications required for efficient and trouble-free operation. The furnace has been installed on the vibration isolation table in conjunction with the laser optical system. The top access cover has a 1/8" x 2" slotted laser port for access to the heat zone. The operation temperature is 1200C. But, by changing the thermocouples and reconfiguring the control systems, it could operate up to 1400C.

#### **IV RESEARCH IMPLEMENTATION**

The principal implementation upon first commissioning of the system is the determination of residual stresses and adhesion, as they relate to microstructure and deposition conditions. Mechanical measurement procedures devised for the brittle films are being used for this purpose. These include Multistrain, Sphere Impression and Direct Compression tests. In these tests, strain measurements made in conjunction with observations of cracking, buckling and spalling allow determination of the adhesion (interface fracture toughness) and the fracture toughness of the film. Independent measurements of the residual stresses in the film as a function of temperature allow distinction between the intrinsic and thermal expansion misfit stresses. Then, the overall residual steady-state and its temperature variation may be integrated with the fracture toughness parameters to establish fail safe design strategies.

**TABLE I****SUMMARY OF AQUISITIONS****INFRARED IMAGING**

Amber Galileo IR Camera	Elliott Rittenberg Amber Represenative 508-558-5650	74,000.
IX $\mu$ scope objective with filter wheel 25 mm IR lens	George Welch Diversified Optics 603-898-1880	7,420 3,990
Thermal Wave Imaging System Control	Steve Shepard Thermal Wave Imaging 810-569-4960	19,875
PC Host Computer	Mike Gipson Micron 800/588-4803	4,268
	<b>TOTAL</b>	<b>\$110,453</b>

**SCANNING PROBE (ATOMIC FORCE) MICRSCOPE**

Dimension 3000 Scanning Probe Microscope with NanoScope IIIa Controller	Digital Instruments 520 East Montecito St. Santa Barbara, CA 93103 800-873-9750	
	<b>TOTAL</b>	<b>\$160,340</b>

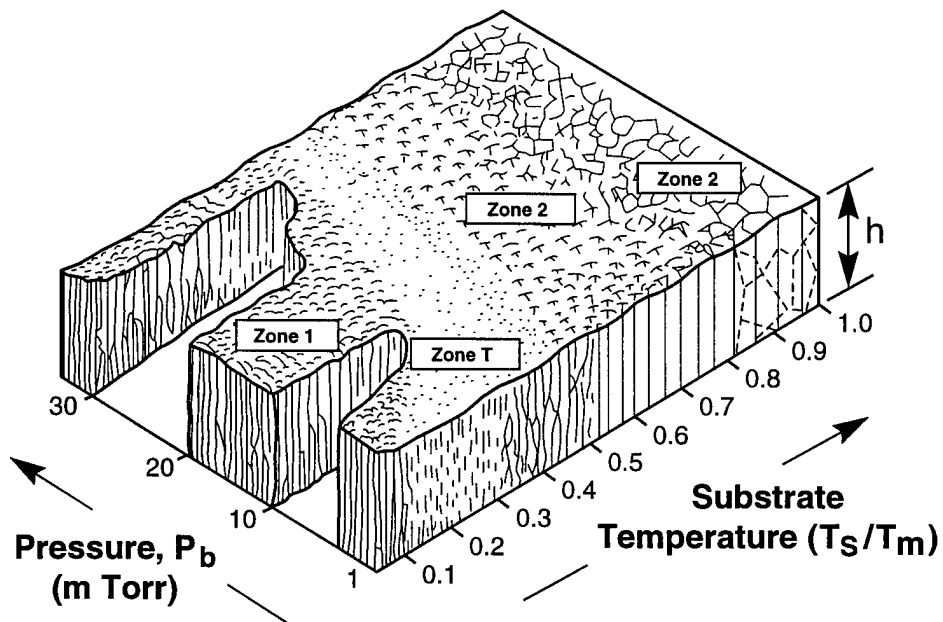
## **Curvature Measurement Equipment**

Optics	Various	24,093.85
Top loading vacuum furnace	Oxy-Gon Industries, Inc.	59,757.00
	PO Box 40	
	Epson, NH 03234	
	603/736-8422	
Vacuum pump Station	Oxy-Gon Industries, Inc.	11,797.00
Gas Purification furnace	Oxy-Gon Industries, Inc.	7,966.00
	<b>TOTAL</b>	<b>\$103,613.85</b>

## **PVD system**

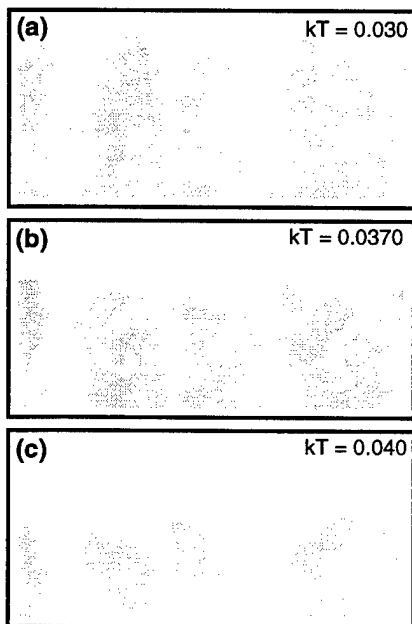
PVD Chamber	PVD Products Inc.	
	4R Alfred Circle	
	Bedford MA 01730	
	(617) 275-9959	
	<b>TOTAL</b>	<b>\$250,000</b>

# MICROSTRUCTURE MODEL



Zone  
Map

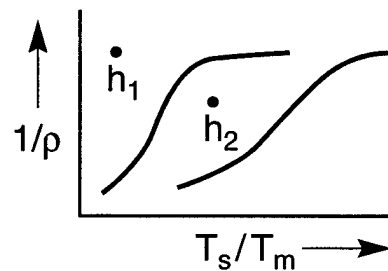
## I Porosity



## M.D. Model

$\dot{h}_s, \rho$

$T_s/T_m$



**CALCULATE**  $\Rightarrow \rho = F[\dot{h}_s, T_s/T_m, P_b]$

- Effects of Ion Bombardment on  $\rho$

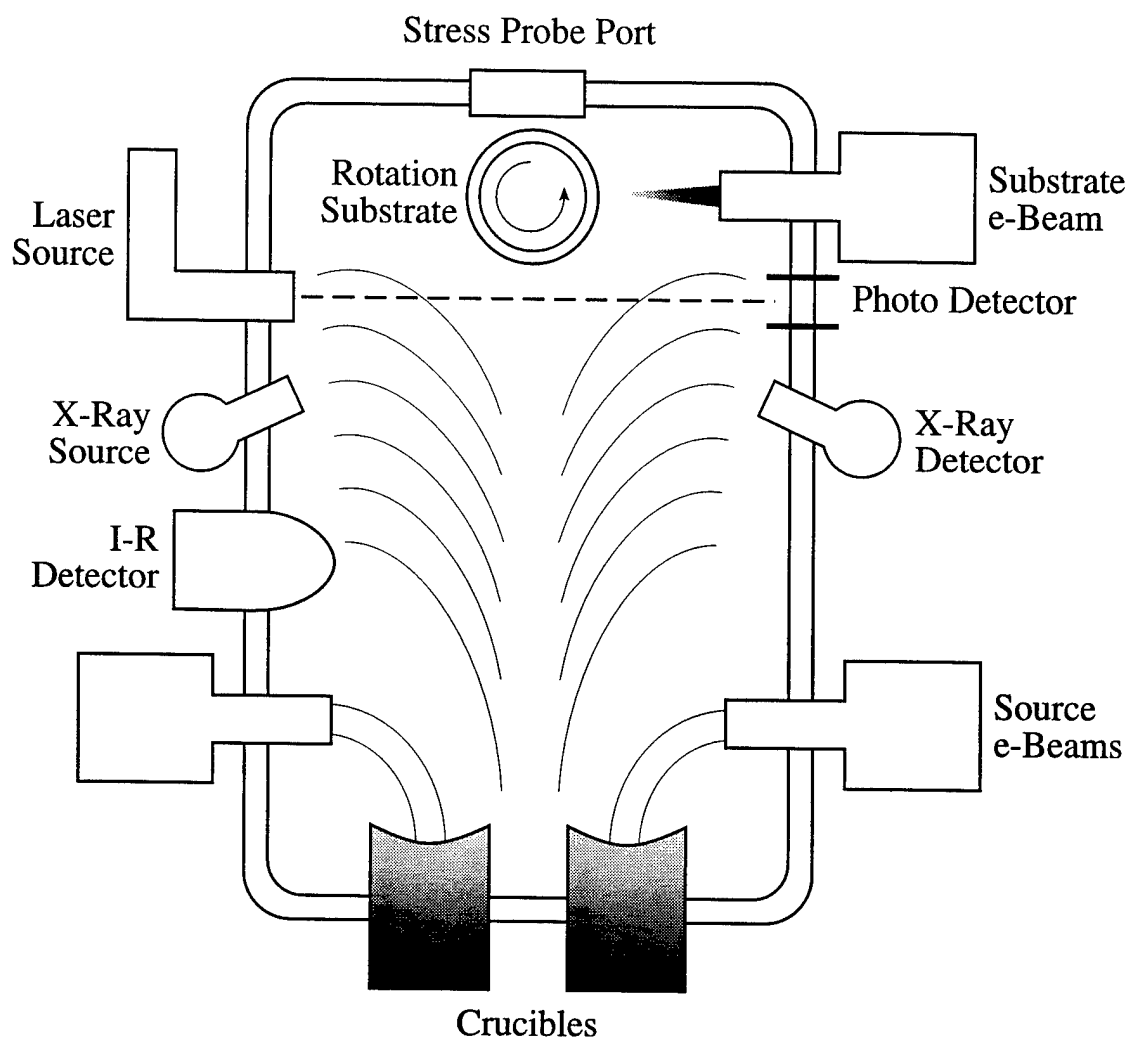


FIGURE 2

# ELECTRON BEAM EVAPORATION

## Source Model

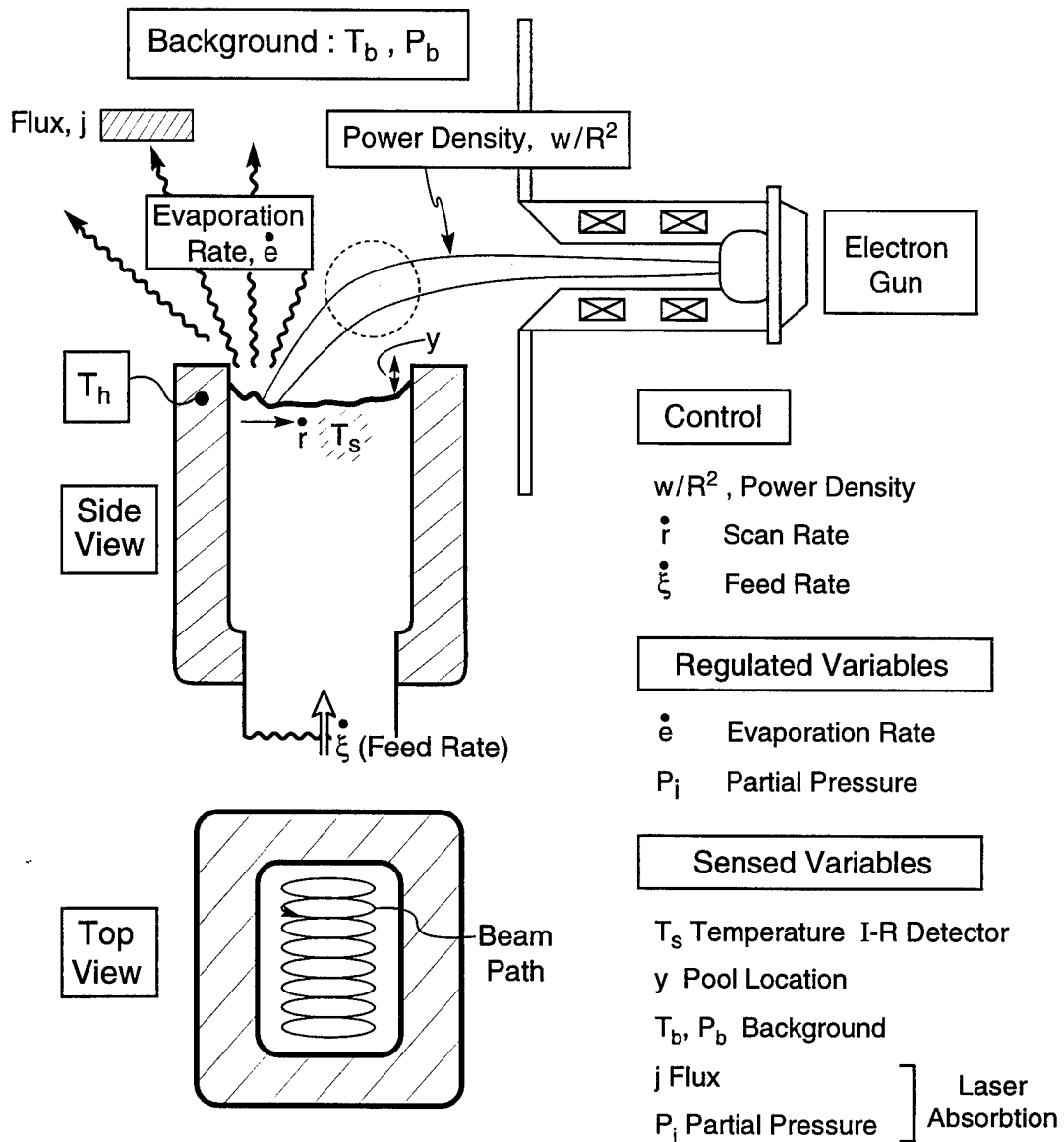


FIGURE 3

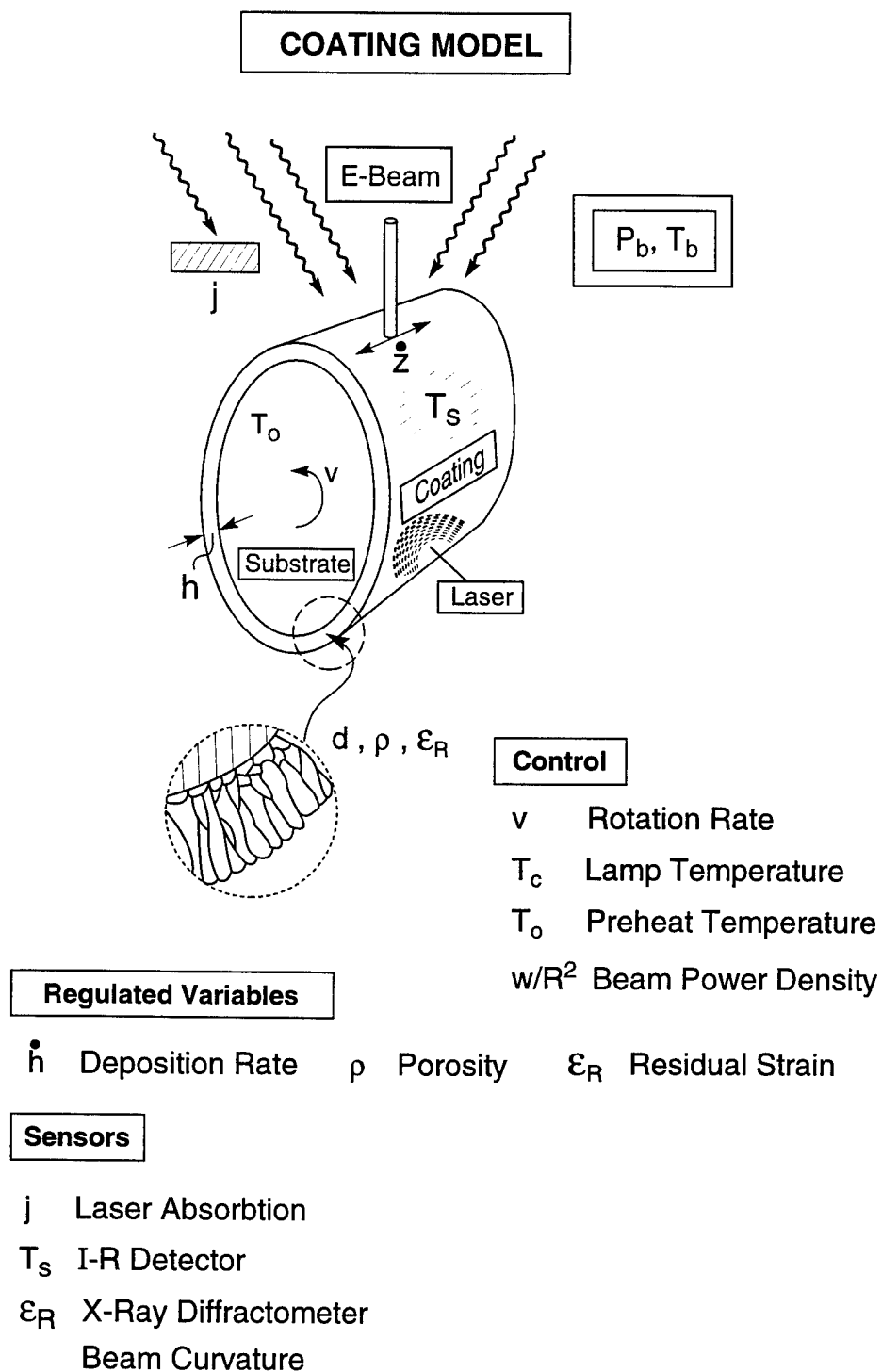


FIGURE 4



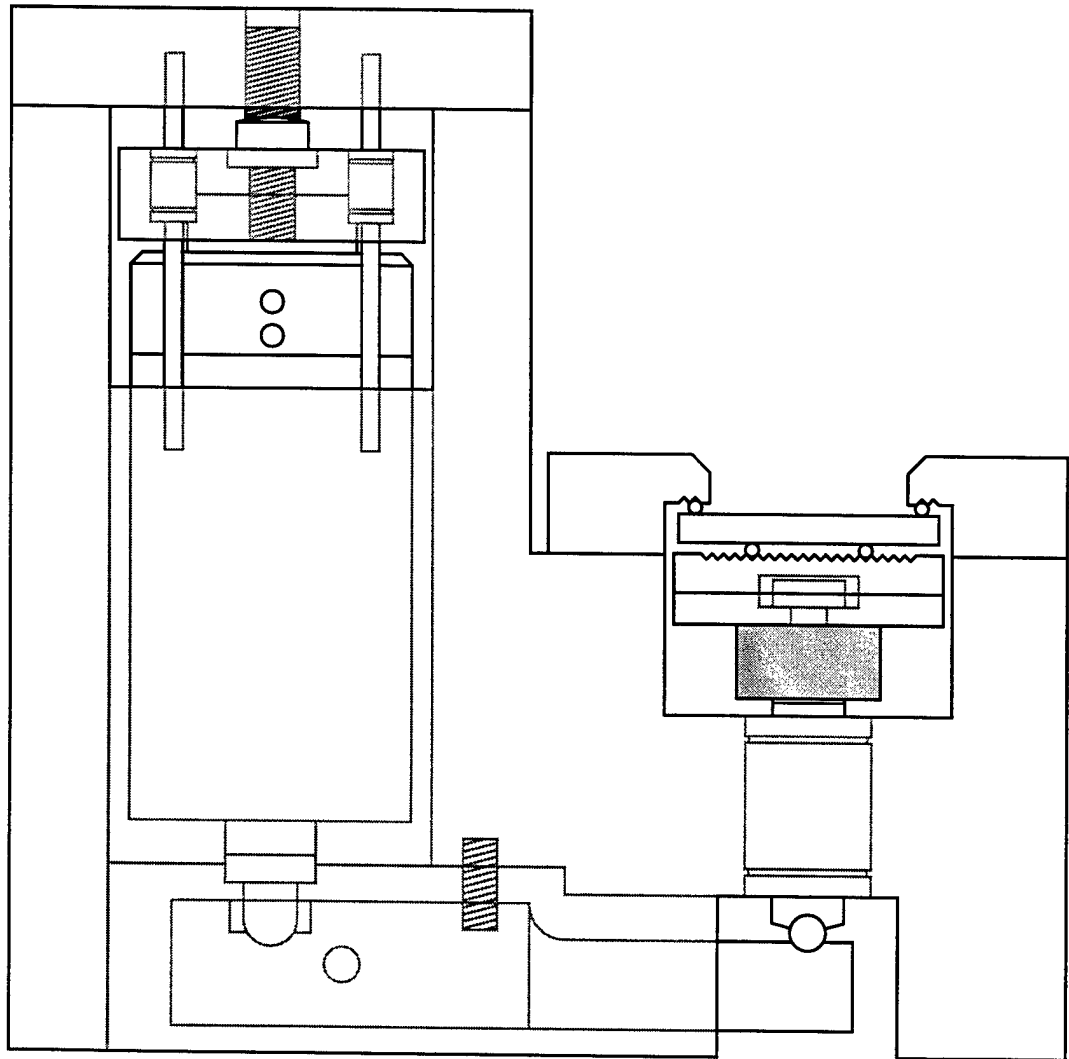


FIGURE 5

# Optical Instrument Layout

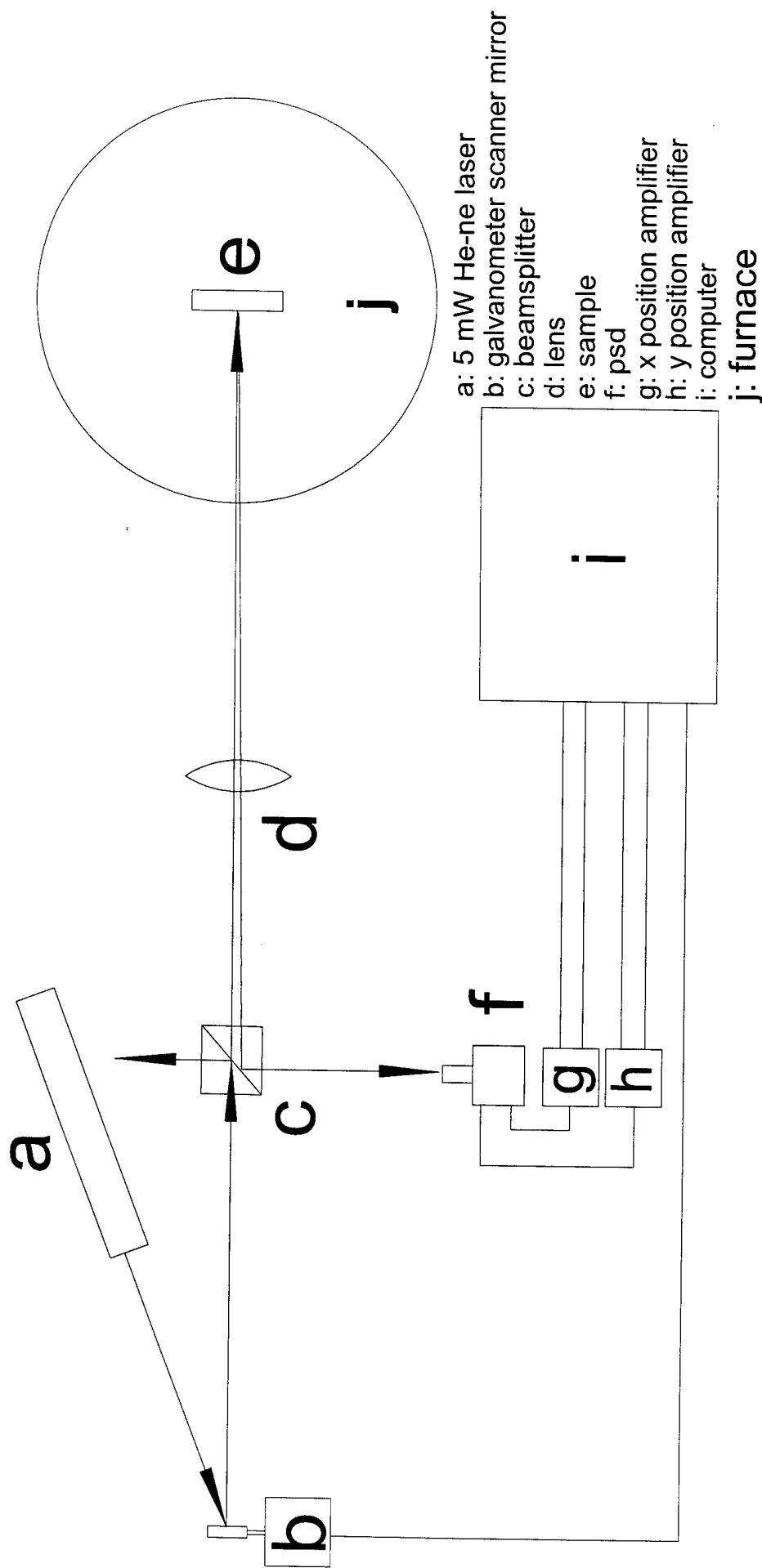


FIGURE 6